THE STRUCTURE OF THE MERCURY LINE, λ 2536

BY
LUCY WILSON

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

BALTIMORE
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The structure of the line of the mercury arc of wave-length 2536.72 A is of special interest because of its remarkable efficiency in exciting "resonance."[1] For the investigation of the structure of this line, a Fabry and Perot interferometer was selected because of the high resolving power attainable with this instrument under proper conditions. The first part of the problem, therefore, consisted in the study of the relative reflecting power and transmission of various thin films in the region of the 2536 line, in order to find that substance which would be most efficient as a coating for the interferometer plates.

I. THE ULTRA-VIOLET INTERFEROMETER

Any interferometer of the Fabry and Perot type depends for its efficiency upon the number of reflections that it is possible to obtain in the region to be investigated, and upon their relative intensities. These two factors depend only upon the reflecting power of the surfaces, as may be seen from Fig. 1 and Table I.

Let *BC* and *DE* (Fig. 1) be the two plates of the interferometer upon which is incident a ray of light whose intensity is represented by 100 after it has traversed the first plate. Assume the reflecting power of the surface to be 30 per cent and the absorption to be zero, then the intensities of the images will be as represented. The first image I_1 is due to the transmitted light which has suffered only one reflection; the second image is produced after three reflections; the third, after five, and so on. The effect on the relative intensities of the images of increasing the reflecting power is apparent from the figures below, which were obtained by calculation from diagrams like Fig. 1.

It is at once evident that, as the reflecting power increases, the ratio of the intensities of the successive images approaches unity.

[1] R. W. Wood, *Philosophical Magazine* (6), **18**, 240, 1909; **23**, 689, 1912; **32**, 329, 1916.

Absorption cuts down the intensity of each transmitted image but does not affect the relative intensities of successive images.

If the reflecting power of the surfaces of the interferometer plates which face each other is f, the relation between the relative

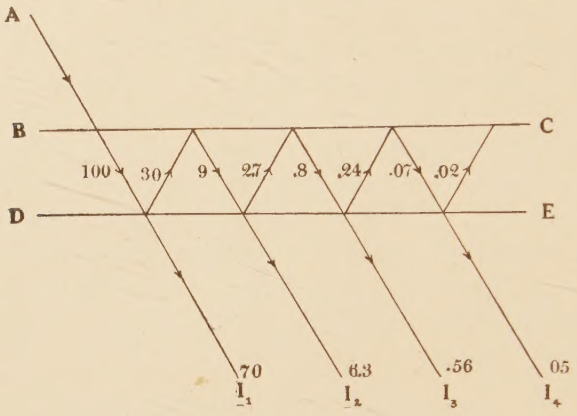


FIG. 1

intensities of the maxima and minima of the fringes produced is given by[1]

$$r = \left(\frac{1-f}{1+f}\right)^2.$$

For example, a value of $f = 74$ per cent gives a value of $r = 0.02$; i.e., the minima are almost black. Thus the definition of the fringes depends entirely upon the reflecting power.

TABLE I

Reflecting Power	30 Per Cent	50 Per Cent	70 Per Cent	80 Per Cent	90 Per Cent
I_1	70.0	50.0	30.0	20.0	10.0
I_2	6.3	12.5	14.7	12.8	8.0
I_3	0.56	3.13	7.2	8.2	6.6
I_4	0.05	1.6	3.6	5.2	5.9

In using thin films, there are two ways in which the reflecting power can be increased: a thin film of a given substance can be made more highly reflecting by making it thicker up to a certain

[1] Fabry and Perot, *Annales de Chimie et de Physique*, **12**, 459, 1897.

limiting point, and a substance of naturally higher reflecting power can be substituted in place of the one under consideration.

Method.—The method of comparing various metals with respect to their efficiency for use in the Fabry and Perot ultra-violet interferometer was a very simple one. Thin films of the substance were deposited on the one-inch quartz plates of the interferometer, and the plates were mounted in the etalon with a wedge-shaped layer of air between them. This was accomplished by inserting a small piece of ordinary writing paper between the plates at a point near their edge, and by bringing the plates into contact at a point 180° removed from the paper, by means of the adjustment screws attached to the mounting of the etalon. Thus multiple images were obtained of any source of light viewed through the plates. The

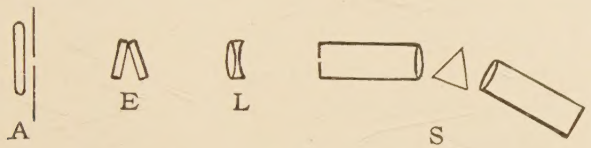


FIG. 2

images in the 2536 line were then photographed. The actual arrangement is represented in Fig. 2. The etalon *E* was mounted at about a meter's distance from the quartz water-cooled mercury arc *A*, in front of which was an aperture of 1 mm diameter. A quartz-fluorite achromatic lens *L*, at a distance of a meter from the etalon, brought the images to a focus on the slit of the quartz spectrograph. In the position of each line of the mercury spectrum, as viewed in the spectrometer and as recorded on the photographic plates, there appeared a series of vertically arranged dots of diminishing intensity. The number of images and the relative brightness of the successive ones were by this means immediately evident. With the films which showed up best by this method, photographs were also taken of the fringes formed when the plates were mounted in the etalon with separations of six and of 10 mm.

Up to this time, silver has been almost universally used in the visible region and nickel in the region of shorter wave-lengths for which the silver failed to give sufficient reflecting power. Cathodi-

cally deposited nickel was used by Fabry and Buisson in their investigation on "Wave-Length Measurements for the Establishment of a System of Spectroscopic Standards," published in the *Astrophysical Journal* of October 1908 (**27**, 169). Their observations extended as far as wave-length 2373. Other observers have also used nickel deposited by cathodic sputtering in the region of wave-lengths slightly longer than that of the 2536 line. The work of Dr. E. O. Hulburt in this laboratory on the "Reflecting Power of Metals in the Ultraviolet Region of the Spectrum"[1] showed that silicon possesses a much greater reflecting power in the regions between 2000 and 3000 A than does nickel. It was, therefore, hoped that silicon might be of use in the present case. Ultimately, films of nickel, silicon, cobalt, aluminum, platinum, silver, gold, and stibnite were prepared and examined.

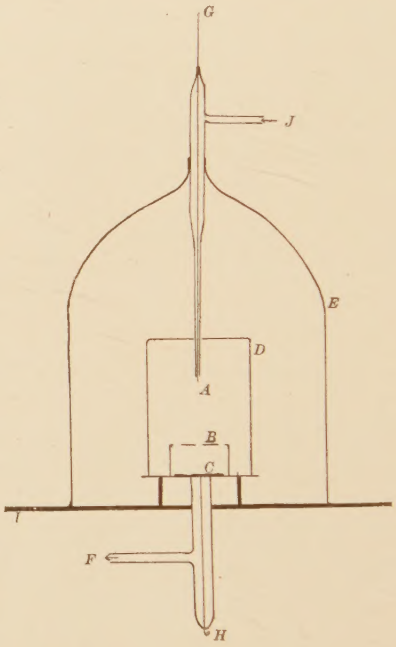


FIG. 3

As many of the films were sputtered cathodically with the same apparatus, a description of it (Fig. 3) in its general form is given here. The large bell-jar *E* was held air-tight against the ground glass plate *I* by means of stopcock grease. To avoid the presence of hydrocarbon vapor, the discharge was confined as nearly as possible to the interior of the inner vessel *D*. The cathode *C* consisted of a large flat piece of the metal to be sputtered (the area was of the order of 10 or 15 sq. cm) and the anode, *A*, was the pointed end of an aluminum rod. The lead wires of both electrodes were incased in glass to prevent the discharge from taking place outside *D*. The

[1] *Astrophysical Journal*, **42**, 205, 1915.

surfaces on which the film was to be deposited were mounted on a glass stand at *B* with their faces toward *C*. Connections to the pump were made through *F* and to the transformer by means of *G* and *H*. The transformer operated on the 110-volt alternating current and gave approximately 26,000 volts across the secondary. The pointed shape of the anode and the large flat cathode caused the rectification to take place always in this direction. A side tube *J* allowed any desired gas to be introduced into the vessel.

Silicon.—The silicon films obtained by cathodic sputtering in the atmosphere of mercury vapor yielded disappointing results in that their absorption for the ultra-violet was large. This was probably due to the presence of a trace of carbon from the stopcock grease, which not only made the films faintly brown in color but also caused them to adhere to the surface upon which they were deposited with such tenacity that they could be removed only by repolishing with rouge. Since it was desired to have not only an efficient ultra-violet interferometer but also one that could be easily prepared, the investigation was abandoned in favor of other substances. Later on, however, some beautifully bright silicon films were loaned to us by Mr. W. F. Meggers of the Bureau of Standards. These films were free from the brownish tint, and their absorption was only that which was to be expected from their thickness. Multiple images with them gave, however, a slightly less favorable ratio of intensities than that obtained from our best nickel films.

Nickel.—The nickel films tested were prepared in three different ways:

a) Films of varying thickness were deposited cathodically in an atmosphere of hydrogen and in air. The sputtering apparatus was arranged as represented in Fig. 3. The inflow of the hydrogen was so regulated that the dark space at the cathode was always maintained tangent to the surfaces of the plates upon which the nickel was being deposited. Good nickel films, i.e., those which are hard and gray and bright, were made in this way.

b) Nickel was distilled in a vacuum from a hot tungsten filament on to the quartz surfaces. A piece of fine tungsten wire was wound into a small spiral, and into this spiral was inserted a small sliver of nickel. *T* (Fig. 4) is the tungsten spiral whose lead

wires A and B connect with a 20-volt circuit containing variable resistance. The quartz plates are at Q and Q'.

In order to obtain films that were fairly hard the receiver was exhausted and the filament was given a preliminary heating before the quartz plates were introduced into the apparatus; this preliminary heating lasted until the nickel melted and a very thin deposit appeared on the walls of the vessel. After the plates were put in, the pump was allowed to run until the McLeod gauge indicated that most of the occluded gases had been given off. The current was then passed through the filament, and its strength increased until the filament reached a white heat. The films produced by this method were of much the same appearance as those deposited cathodically but were not as hard as the best cathodic ones. There was little difference in the behavior of the two sets of films.

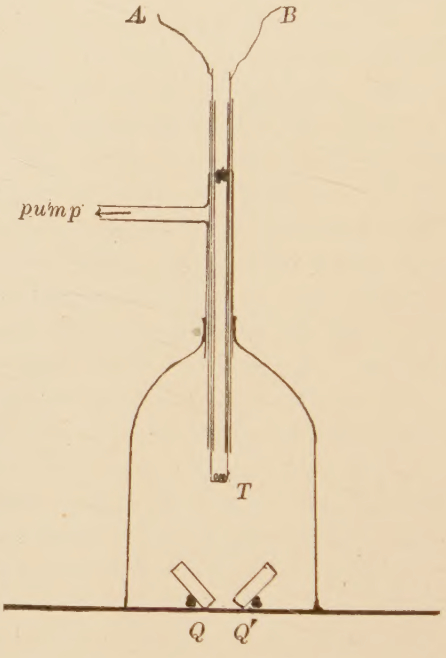


FIG. 4

c) A thin layer of nickel was electroplated from a solution of nickel fluorborate[1] on various foundations. For an initial layer, hard cathodic nickel was found to yield the best results. Nickel on gold and nickel on silver had a fair reflecting power but large absorption. The nickel distilled in vacuo was rather soft and inclined to frill as soon as the plate was removed from the electroplating solution. The films which gave the most favorable ratio of intensities in the multiple images and those which were finally

[1] A. Hollard, *Science Abstracts*, 15, 558, 1912.

used in the work on the determination of the structure of the 2536 mercury line were made by electroplating upon a cathodic foundation. In order to insure hardness in the initial layer, the sputtering apparatus was arranged a little differently. The positions of the cathode and anode were interchanged, and the plates were covered with a piece of thin, sheet tin, and the discharge was allowed to run for two hours until its appearance indicated that little occluded gas was being given off. The tin was then removed by means of an electromagnet and the discharge continued for half an hour.

In the electroplating, the difficulty encountered was the production of a non-uniform layer owing to the greater density of the current near the surface of the liquid than at a short distance below it. This was in part compensated for by inclining the plate and in part by plunging the plate into the solution and slowly drawing it out, repeating the process several times until the film possessed the desired thickness.

This electroplated layer increased the reflecting power without increasing the relative absorption, i.e., a film made according to this last method possessed, with a given absorption, greater reflecting power than one of the same absorption made by either of the other two methods. These films were hard enough to permit polishing with rouge on a bit of cotton, but the process had little effect on the reflecting power.

Cobalt.—Cobalt of three different thicknesses was deposited cathodically in an atmosphere of hydrogen. The method was the same as that described under (*a*) for nickel. A thick film made by sputtering two and three-quarter hours showed good reflecting power but large absorption. A much thinner film, one made by running the discharge only thirty minutes, proved to be almost as efficient in the ultra-violet as the silicon and the electroplated nickel. A film of thickness intermediate between these two (i.e., one for which the sputtering lasted for one and one-half hours) gave less favorable relative intensities than the thin film. An interesting fact noted in connection with these cobalt films was that if a little moisture was deposited on them from the fingers (or elsewhere) the metal frilled and assumed the properties of matt surfaces.

Platinum.—This metal was sputtered cathodically in air and films of two different thicknesses were made and tested. The results showed them to be less desirable than the cobalt.

Aluminum.—From the work of Dr. Hulburt, mentioned above, it appears that as a reflector in the ultra-violet aluminum is second only to silicon. Like silicon, too, it is difficult to obtain in the form of a film. Experiments conducted by V. Kohlschütter and R. Miller[1] and by F. Fischer and O. Hähnel[2] on the "Kathodic Volatilization of Metals in Rarefied Gases" show that the presence of helium accelerates the volatilization of aluminum to a certain extent, and that argon greatly increases the rapidity of the process.

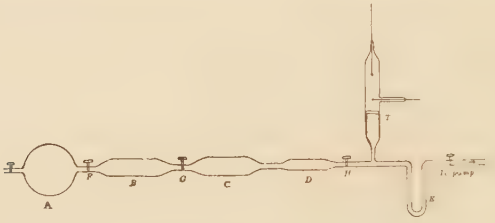


FIG. 5

Therefore the method used in this case was that of cathodic sputtering in argon. An entirely different form of apparatus from that previously described was made use of. It is represented in Fig. 5. The electrodes used in the discharge tube *T* consisted of small lumps of aluminum welded on German silver wire and placed at a distance of about 4 inches apart. The quartz plates (one at a time) were held in position an inch below the lower electrode. (Preliminary experiments with this distance, equal to 1 centimeter, showed decided non-uniformity in the deposit.) This tube was connected with a T-tube, one arm of which joined it to the pump through a U-tube immersed in liquid air and the other arm to the argon bulb *A* through a series of purifying agents. The bulb *B* contained calcium to remove the nitrogen; *C* contained cuprous oxide to remove the oxygen; and *D*, phosphorous pentoxide for absorbing water vapor. The secondary of an induction coil was connected to the electrodes.

[1] *Zeitschrift für Elektrochemie*, **12**, 365, 1906.

[2] *Ibid.*, **14**, 366, 1908.

The tube T was pumped out until the vacuum was such that the dark space was about 3 mm long. Until the final step in the procedure the connections from the induction coil were so made that the upper electrode was the cathode. The stopcocks G and H were open so that the tubes B, C, and D might be pumped out. When the pressure in T had reached its former value (as indicated by the appearance of the discharge), G and H were once more closed, and F opened for an instant to allow a small quantity of argon to flow into B. The tube B was then heated with a Bunsen burner until the calcium glowed. The stopcock G was next opened and the gas allowed to come in contact with the CuO which was also heated and with the P_2O_5. Upon opening the last stopcock H the gas flowed into the tube T, where it caused a marked change in the appearance of the discharge, due to the increase in pressure and to its characteristic spectrum. Observations with a direct-vision spectroscope showed that hydrogen was always present. This was, in all probability, given off by the aluminum electrodes. The tube was washed out with argon several times in the manner described above, the process lasting from half an hour to an hour. Then a heavy current was applied until the cathode (still the upper electrode) glowed to redness. When this condition was reached, the current was reversed until the lower electrode (now the cathode) reached red heat. The strength of the current in the primary was then reduced to half its former value and so maintained while the deposition took place. The deposit began suddenly, accompanied by marked changes in the appearance of the discharge. Before the cathode reached a temperature sufficient to cause it to glow, the predominating color of the discharge was a pale, whitish lavender; as the temperature of the cathode rose, the luminosity assumed a deeper violet hue; and just before the deposition began the color changed from this deep-blue violet to a bright rose color, which was very brilliant near the cathode, and shaded off to a pale violet in the region of the anode. Three minutes after this marked change took place the films were thick enough.

Though these films were brilliant in visible light and highly reflecting in the ultra-violet, experiments showed them to be slightly less efficient than the electroplated nickel.

Silver and gold.—Films of these two metals were sputtered cathodically in order to be able to make certain comparisons in the visible regions and to gauge some of the governing conditions from the various methods, and in the different forms of apparatus.

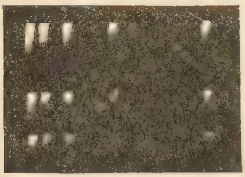
Stibnite.—Because of its remarkable optical properties it was thought that possibly this substance (sulphide of antimony) might prove of value. However, a film of stibnite obtained by cathodic deposit exhibited a very low reflecting power.

From a comparison of the photographs made with the various kinds of films and a consideration of the experimental difficulties involved in preparing the films, it was decided that nickel electroplated upon a cathodic foundation of nickel was best suited for the present investigation. The films used were, therefore, those described on page 345.

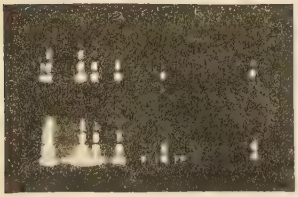
Every substance that offered any possibility of possessing high reflecting power in the ultra-violet was tried, but even the best films were most disappointing in the results which they yielded. The largest number of images ever photographed at the 2536 line was four, with the estimated intensity ratio given by a reflecting power of 40 per cent. In Fig. 6, a comparison of the images in the visible lines, photographed with silver films, with those obtained at the 2536 line with the best nickel films shows the relatively poor reflecting power of the latter in the ultra-violet region.

II. THE STRUCTURE OF THE 2536 MERCURY LINE

Method.—The method of using the Fabry and Perot interferometer in order to determine the difference in wave-length of two radiations situated very close together consists simply in finding the difference of path which corresponds to a position of "complete disagreement" or "dissonance" and of ascertaining whether this special path-difference represents the first time this condition has occurred as the plates are separated after being in contact. In the case of the Michelson interferometer, when dissonance occurs for a double line, the fringes disappear completely, if the lines are of equal intensity. In the Fabry and Perot interferometer, dissonance is indicated by a system of fringes with a spacing equal to one-half

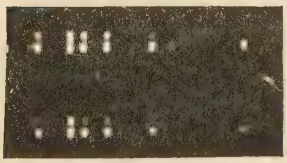


Electroplated Nickel



Silicon

Cobalt



Aluminum

Silver

FIG. 6

of that which obtains for zero path-difference. As the path-difference is increased from zero position, the fringes first widen, then double, and finally form an equally spaced system of one-half the original interval.

With visible light, where the wave-lengths of the two radiations are widely different, one can easily watch the fringes get into step and out again, and the position in which one set of fringes is situated exactly between pairs of the other set can be estimated by the eye. For work in the ultra-violet it is, of course, necessary to make use of photography.

The same arrangement of apparatus was used as that indicated in Fig. 2, except that the interferometer was substituted for the etalon, and the screen removed from its position in front of the arc. The distance from the arc to the interferometer plates was about 60 cm, and the lens was placed a meter and a quarter from the interferometer plates. When the fringes were in focus on the slit of the spectrograph $LD = 51$ cm.

For this work, where it is necessary to have a variable path-distance the etalon was discarded and a mounting substituted by which the plate nearer the arc could be made to approach or recede from the other plate by steps as small as a hundredth of a millimeter. This was accomplished by means of a fixed screw with graduated head and a movable nut on which the one plate of the interferometer was mounted. It was found necessary to diaphragm the interferometer to an aperture of 9 mm because of non-uniformity in the films.

The first step in the procedure consisted in determining the position of contact of the plates. They were then separated by 1 mm and adjustments for parallelism were made for the visible region, i.e., either with a ground glass plate interposed between the arc and the interferometer or with a cell containing neodymium nitrate, which lets through only the green line. When the adjustments were completed, the absorbing screen was removed and the fringes photographed. The same process was repeated for each millimeter up to seventeen. The times of exposure varied from forty-five seconds to five minutes. An exposure of three minutes showed on the average the best contrast.

RESULTS

In the trial experiments with the etalon, the best films of several of the metals showed the fringes in the 2536 line double when the separation was 10 mm. The subsequent work with the electroplated nickel films showed that the fringes in this line were single at a separation of 9 mm and again at 13 mm, but for all intermediate points they were double, and the position of complete disagreement came at a separation of 11.7 mm. The region from zero path-difference up to this point was then examined in half-millimeter steps. No sign of doubling could be detected, and it was therefore concluded that 11.7 mm was the position of the *first* complete disagreement. Investigation was then continued beyond 13 mm up to 2 cm. The fringes gradually faded away into invisibility.

Hence the conclusion is that the line is a doublet, each component of which has a finite width. These results correspond to a Michelson visibility-curve of the form shown in Fig. 7.

Intensity-curve Visibility-curve

FIG. 7

The possibility of the foregoing intensity-curves being due to reversal instead of to a true double line was ruled out by the following experiments. Photographs which were made with a "mercury resonance bulb" duplicated the observations given by the arc. A mercury resonance bulb consists simply of a quartz bulb containing mercury vapor at room temperature, illuminated by light from a quartz mercury arc. Under these conditions the bulb emits a monochromatic radiation of wave-length 2536 which is designated as "resonance radiation." In this case, the mercury vapor present was less dense than in the arc. The water-cooled mercury arc, as it was always used, was flanked on either side by the coils of an electromagnet which deflected the arc forward on to the

quartz window in order to diminish the absorption effect as much as possible. For the purpose of the present experiments, the direction of the current in the magnet was reversed and long exposures (i.e., two to three hours) were made, with the result that no trace of the fringes and only a faint trace of the line itself was discernible. Therefore, a change in possible absorption does not change the intensity-curve, i.e., the relative intensities of the two components remain unaltered.

Calculations of the wave-lengths of the components.—Let the fringes of wave-lengths λ and $(\lambda+a)$ be in position of complete disagreement and let $\Delta =$ the path-difference.

Then $\Delta = 2e$, where e is the thickness of the air film between the plates.

If the order of interference is p, then the pth fringe of rays of wave-length $(\lambda+a)$ lies in the center between the pth and the $(p+1)$th fringes of the rays of wave-length λ.

The pth fringe of the rays λ corresponds to a difference of path Δ and the pth fringe of the rays $(\lambda+a)$ corresponds to the path-difference $\left(\Delta+\frac{\lambda}{2}\right)$. Therefore

$$p=\frac{\Delta}{\lambda}=\frac{\Delta+\frac{\lambda}{2}}{\lambda+a},$$

and

$$\frac{a}{\lambda}=\frac{\lambda}{2\Delta}=\frac{1}{2p}.$$

Applying the results obtained from the experiments to this last equation gives

$$\frac{a}{\lambda}=\frac{2536.72\times 10^{-7}}{46.8},$$

$$a=\frac{(2536.72\times 10^{-7})^2}{46.8}=14\times 10^{-10}.$$

Therefore the results given by the Fabry and Perot interferometer lead to the conclusion that the 2536 mercury line is a doublet, the components of which are separated by 0.014 A. To determine

the probably more complicated structure of this line, an instrument of greater efficiency than the Fabry and Perot interferometer is necessary.

This problem was undertaken at the suggestion of Professor Wood, and the investigation was carried on under his direction. To him I wish to extend my thanks for his unfailing interest as well as for his invaluable help.

I wish to express my gratitude to Professor Ames, whose kindly interest has been continually manifest; and to Dr. Pfund and Dr. Anderson for many helpful suggestions; also to Mr. Meggers for making the silicon films.

JOHNS HOPKINS UNIVERSITY
June 1917

BIOGRAPHICAL NOTE

Lucy Wilson, daughter of John J. S. Wilson, Jr., and Lucy (White) Wilson, was born in Bloomington, Illinois, on October 19, 1888. Until the time of her entrance into Wellesley College in September, 1905, her education was conducted in the public schools of her native city. In June 1909 the degree of B.A. was conferred upon her by Wellesley College, and in the autumn of that year she went to Mt. Holyoke College as assistant in the department of physics. For two years she held this position, and for two years she was instructor in physics at the same institution. She entered Johns Hopkins University as a graduate student in physics in October 1914 and attended graduate courses given by Professors Ames, Wood, Anderson, Jones, and Cohen. During the year 1914–15 she was a Johns Hopkins University Scholar, and during the year 1916–17 she held one of the Johns Hopkins University Fellowships.